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Mean field theory of percolation with application to surface effects

K De'Bell† and J W Essam

Mathematics Department, Westfield College, University of London, London NW3 7ST, England

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Abstract. A probabilistic formulation of mean field theory for percolation in a general medium is given. The theory covers the whole density range and, above the critical density, provides the necessary generalisation of the random walk approximation. Application to surface percolation enables the calculation of scaling functions and critical exponents for the ordinary, surface, special and extraordinary transitions considered by previous authors in the context of ferromagnetism.

1. Introduction

A general percolation model which includes both continuum and lattice percolation has been formulated by Coniglio and Essam (1977). The model was one in which particles were distributed with density $\rho(\boldsymbol{r})$ through a region Ω. With each point of Ω a 'capture' region $\omega(\boldsymbol{r})$ was defined and a particle at $\boldsymbol{r}'$ was said to be reachable in a single step from a particle at $\boldsymbol{r}$ if $\boldsymbol{r}' \in \omega(\boldsymbol{r})$. Low-density expansions for the pair connectedness were derived.

Here we introduce a 'field' variable $h(\boldsymbol{r})$ into the model which allows the properties of the percolating region above the critical density to be obtained. The mean field approximation is formulated and applied to systems in which properties such as the percolation probability and mean cluster size are spacially varying. Surface percolation is considered as an example of such a system and results which correspond to those of Lubensky and Rubin (1975) and Bray and Moore (1977) for the surface properties of a magnetic system are obtained. In particular it is found that the four types of transition described by the above authors also occur in percolation theory. A general solution of the mean field equation is obtained and scaling forms corresponding to the ordinary, surface, special and extraordinary transitions are extracted. The critical exponents for these transitions are summarised in table 1.

Theumann (1979) and Carton (1980) have previously obtained results for surface percolation as a limiting case of the Potts model. Their approach is field theoretical and the mean field equation is obtained as a natural extension of that for the Ising model. A similar equation is obtained here using only probabilistic arguments. Our equation agrees with that of Theumann in the leading terms of the expansion which determine the critical behaviour but, not surprisingly, differences occur when the order parameter is no longer small.

† Now at Department of Physics, University of Edinburgh, Edinburgh EH9, Scotland.

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Table 1. Critical exponents.

	Ordinary	Surface	Special	Extraordinary
$\gamma_{11} = \gamma'_{11}$	$-\frac{1}{2}$	1	$\frac{1}{2}$	-3†
$\gamma_1 = \gamma'_1$	$\frac{1}{2}$	1	1	-1†
β_1	$\frac{3}{2}$	1	1	3

† γ_1^e and γ_{11}^e are not defined (see text).

Theumann's work was concerned only with the exponent β_1 of the percolation probability. His results agree with ours except in the case of the extraordinary transition. The discrepancy is due to a difference in definition. We take the exponent of the leading order discontinuity (following Bray and Moore (1977)) whereas Theumann takes the exponent of the continuous part (following Lubensky and Rubin (1975)). Our value is the one which should be used in scaling relations.

Carton (1980) obtains the mean size exponent γ_1 (as well as β_1) for the ordinary transition and extends the mean field results, which are only valid above the critical dimension $d_c = 6$, by calculating the coefficient of $\varepsilon (= 6 - d)$ in the epsilon expansion below d_c.

2. General formulation

The model and its associated functions will now be defined and the general mean field theory equations will be derived.

2.1. Definitions

In percolation theory the field $h(\boldsymbol{r})$ which is the analogue of a magnetic field in a spin system may be defined by the introduction of 'impurity' particles (Essam 1980). These particles are distributed independently through Ω with density $\nu(\boldsymbol{r})$, and $h(\boldsymbol{r})$ is the expected number of such particles in the capture region $\omega(\boldsymbol{r})$, thus

$$h(\boldsymbol{r}) = \int_{\boldsymbol{r}' \in \omega(\boldsymbol{r})} \nu(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}'. \tag{2.1}$$

We shall see that $h(\boldsymbol{r})$ plays a similar role to the occupation probability of the 'ghost' site used by other authors (Griffiths 1967, Kasteleyn and Fortuin 1969, Reynolds *et al* 1977). The term particle when unqualified, will refer to the ordinary particles which have density $\rho(\boldsymbol{r})$.

A particle at $\boldsymbol{r}'$ is said to be connected to a particle at $\boldsymbol{r}$ if there is a sequence of particles with vectors $\{\boldsymbol{r}_0 = \boldsymbol{r}, \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_l = \boldsymbol{r}'\}$ such that $\boldsymbol{r}_i \in \omega(\boldsymbol{r}_{i-1})$. Let the cluster $c(\boldsymbol{r})$ at the point $\boldsymbol{r}$ be the set of all particles connected to a particle placed at $\boldsymbol{r}$ and let $\omega_c(\boldsymbol{r})$ be the region occupied by this cluster, thus

$$\omega_c(\boldsymbol{r}) = \bigcup_{i \in c(\boldsymbol{r})} \omega(\boldsymbol{r}_i). \tag{2.2}$$

The percolation probability $P(\boldsymbol{r})$ is the probability that $\omega_c(\boldsymbol{r})$ is unbounded or contains

at least one impurity particle;

$$P(\boldsymbol{r}) = 1 - pr(\omega_c(\boldsymbol{r}) \text{ is bounded and contains no impurity particle})$$

$$P(\boldsymbol{r}) = 1 - \left\langle \exp\left(- \int_{\boldsymbol{r}' \in \omega_c(\boldsymbol{r})} \nu(\boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}' \right) \right\rangle_F \tag{2.3}$$

where $\langle \ldots \rangle_F$ is an average over configurations of ordinary particles giving zero weight to configurations in which $\omega_c(\boldsymbol{r})$ is unbounded (F = finite).

The pair connectedness $C(\boldsymbol{r}|\boldsymbol{r}_0)$ may be defined as the probability that a particle placed at $\boldsymbol{r}$ will be connected to a particle placed at $\boldsymbol{r}_0$ and $\omega_c(\boldsymbol{r}_0)$ is bounded and contains no impurity particle. This may be related to $P(\boldsymbol{r}_0)$ by defining an indicator

$$\gamma_c(\boldsymbol{r}, \boldsymbol{r}_0) = \begin{cases} 1 & \text{if } \boldsymbol{r} \in \omega_c(\boldsymbol{r}_0) \\ 0 & \text{if not} \end{cases} \tag{2.4}$$

so that

$$C(\boldsymbol{r}|\boldsymbol{r}_0) = \langle \gamma_c(\boldsymbol{r}, \boldsymbol{r}_0) E_c(\boldsymbol{r}_0) \rangle_F \tag{2.5}$$

where $E_c(\boldsymbol{r})$ is the exponential factor in (2.3) and may be written

$$E_c(\boldsymbol{r}) = \exp\left(- \int \nu(\boldsymbol{r}') \gamma_c(\boldsymbol{r}', \boldsymbol{r})\, \mathrm{d}\boldsymbol{r}' \right). \tag{2.6}$$

If we suppose that $\nu(\boldsymbol{r}')$ includes a 'probe' density $\eta\delta(\boldsymbol{r}' - \boldsymbol{r})$ then

$$C(\boldsymbol{r}|\boldsymbol{r}_0) = \frac{\mathrm{d}}{\mathrm{d}\eta} P(\boldsymbol{r}_0) \Big|_{\eta = 0} \tag{2.7}$$

The mean size $S(\boldsymbol{r})$ of the cluster at $\boldsymbol{r}$ is the expected volume of $\omega_c(\boldsymbol{r})$ in units of $v(\boldsymbol{r}) = |\omega(\boldsymbol{r})|$ given that it is finite and is related to the pair connectedness by

$$S(\boldsymbol{r}) = \frac{\langle |\omega_c(\boldsymbol{r})| E_c(\boldsymbol{r}) \rangle_F}{v(\boldsymbol{r})(1 - P(\boldsymbol{r}))} = \frac{\langle \int \gamma_c(\boldsymbol{r}', \boldsymbol{r}) E_c(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}' \rangle_F}{v(\boldsymbol{r})[1 - P(\boldsymbol{r})]}$$

$$= \frac{1}{v(\boldsymbol{r})[1 - P(\boldsymbol{r})]} \int C(\boldsymbol{r}'|\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}'. \tag{2.8}$$

If ν is constant then

$$S(\boldsymbol{r}) = -\frac{1}{v(\boldsymbol{r})} \frac{\mathrm{d}}{\mathrm{d}\nu} \ln(1 - P(\boldsymbol{r})) \tag{2.9}$$

and if also $v(\boldsymbol{r}) = v$ for all $\boldsymbol{r}$ the $h(\boldsymbol{r}) = \nu v = h$ and

$$S(\boldsymbol{r}) = -\frac{\mathrm{d}}{\mathrm{d}h} \ln(1 - P(\boldsymbol{r})). \tag{2.10}$$

2.2. Mean field approximation

In the limit $\rho(\boldsymbol{r}) = 0$, $P(\boldsymbol{r}) = 1 - \mathrm{e}^{-h(\boldsymbol{r})}$ and an extension to non-zero density may be attempted by replacing $h(\boldsymbol{r})$ by an effective field $h'(\boldsymbol{r})$. This field is obtained by counting ordinary particles whose cluster is unbounded as impurity particles thus let

$$\nu'(\boldsymbol{r}) = \nu(\boldsymbol{r}) + \rho(\boldsymbol{r}) P(\boldsymbol{r}) \tag{2.11}$$

and

$$h'(\boldsymbol{r}) = h(\boldsymbol{r}) + \int_{\boldsymbol{r}' \in \omega(\boldsymbol{r})} \rho(\boldsymbol{r}')P(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'. \tag{2.12}$$

The percolation probability is approximated by

$$\begin{aligned} P(\boldsymbol{r}) &= 1 - \mathrm{e}^{-h'(\boldsymbol{r})} \\ &= 1 - \exp(-h(\boldsymbol{r})) - \int_{\boldsymbol{r}' \in \omega(\boldsymbol{r})} \rho(\boldsymbol{r}')P(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'. \end{aligned} \tag{2.13}$$

Carrying out the η derivative defined in § 2.1 the mean field theory for the pair connectedness is

$$C(\boldsymbol{r}|\boldsymbol{r}_0) = (1 - P(\boldsymbol{r}_0))\left(\gamma(\boldsymbol{r}, \boldsymbol{r}_0) + \int_{\boldsymbol{r}' \in \omega(\boldsymbol{r}_0)} C(\boldsymbol{r}|\boldsymbol{r}')\rho(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'\right) \tag{2.14}$$

where

$$\gamma(\boldsymbol{r}, \boldsymbol{r}_0) = \begin{cases} 1 & \text{if } \boldsymbol{r} \in \omega(\boldsymbol{r}_0) \\ 0 & \text{if not.} \end{cases} \tag{2.15}$$

It is interesting to note that in the non-percolating region ($P(\boldsymbol{r}) = 0$) equation (2.14) is that satisfied by the generating function for random walks. In this region the approximation is equivalent to keeping only the chain graphs in the low-density expansion of Coniglio and Essam (1977). In the percolating region the approximation may be thought of as a random walk model in which the steps belong to a bounded cluster with no impurities.

3. Solution for a homogeneous system

Assume now that $h(\boldsymbol{r})$, $\rho(\boldsymbol{r})$ and $\omega(\boldsymbol{r})$ are independent of $\boldsymbol{r}$ ($= h, \rho$ and ω respectively) so that the percolation probability P is the same for all points. Also let v be the volume of ω and $n(= \rho v)$ be the expected number of ordinary particles in the capture region of a given particle. The equation which determines P is then

$$\ln(1 - P) = -h - nP \tag{3.1}$$

and when $h = 0$ the only solution for $n \leqslant 1$ is $P = 0$. However, when $n > 1$ there is a second solution P_0 which has the property

$$P_0 \cong 2(n-1) \qquad n \to 1^+ \tag{3.2}$$

as may be seen by expanding the logarithm in (3.1). Writing $P = |n-1|\hat{P}$ we find

$$\pm\hat{P} - \tfrac{1}{2}\hat{P}^2 + \mathrm{O}(n-1) = -h/(n-1)^2 \tag{3.3}$$

and provided that n is sufficiently close to 1, $\hat{P}$ depends on $\hat{h} = h/(n-1)^2$ and P is of the scaling form

$$P = |n-1|\hat{P}_{\pm}(\hat{h}) \tag{3.4}$$

where

$$\hat{P}_{\pm}(\hat{h}) = \pm 1 + (1 + 2h)^{1/2} \tag{3.5}$$

and $\hat{P}_+$ refers to $n > 1$. Differentiating with respect to h gives the 'zero field' mean size as

$$S \cong |n-1|^{-1} \tag{3.6}$$

and with the usual definition of critical exponents for percolation (Essam 1980), equation (3.4) yields $\beta = 1$, $\gamma = \gamma' = 1$, $\Delta = \Delta' = 2$ and $\delta = 2$.

The pair connectedness for the homogeneous system may be found by Fourier transformation of (2.14) since $C(\boldsymbol{r}|\boldsymbol{r}')$ depends only on $\boldsymbol{r} - \boldsymbol{r}'$, thus

$$\tilde{C}(\boldsymbol{k}) = \theta(\boldsymbol{k})[(1-P)^{-1} - n\theta(\boldsymbol{k})]^{-1} \tag{3.7}$$

where

$$\begin{aligned}\theta(\boldsymbol{k}) &= \frac{1}{v}\int_{\boldsymbol{r}' \in \omega(\boldsymbol{r})} \exp[-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}'-\boldsymbol{r})]\,\mathrm{d}\boldsymbol{r} \\ &= 1 - \tfrac{1}{2}k^2R^2 + \mathrm{O}(k^4) \qquad k \to 0.\end{aligned} \tag{3.8}$$

In making the expansion, the region ω is assumed to have cubic symmetry and R^2 is the mean value of $(r'_\alpha - r_\alpha)^2$ over the capture region. In the scaling limit when $kR \ll 1$

$$\tilde{C}(\boldsymbol{k}) \simeq \frac{2}{nR^2(k^2 + \xi^{-2})} \tag{3.9}$$

where the connectedness length ξ is determined by

$$\xi = |n-1|^{-1/2} X(\hat{h}) \tag{3.10}$$

with

$$X(\hat{h}) = (\tfrac{1}{2}n)^{1/2} R(1 + 2\hat{h})^{-1/4} \tag{3.11}$$

and we have assumed $\xi \gg R$. In particular

$$\xi^2 = \tfrac{1}{2}nR^2 \begin{cases} |n-1|^{-1} & h = 0 \text{ and } n \neq 1 \\ (2h)^{-1/2} & n = 1 \text{ and } h \neq 0 \end{cases} \tag{3.12}$$

so that the critical exponents associated with ξ are $\nu = \nu' = \frac{1}{2}$ and $\nu_c = \frac{1}{4}$.

4. Solution for a system which has translational sysmmetry in $d-1$ dimensions

Now consider a d-dimensional system in which the percolation probability is independent of all coordinates except one: the z coordinate. Examples of such systems are (i) an infinite system in which ρ or h (or both) are given functions of z, (ii) an infinite system with h and ρ constant but with surface density ρ_1 and 'field' h_1 on the special plane $z = 0$, (iii) a semi-infinite system ($z \geqslant 0$) of constant density ρ and 'field' h, with or without a density and field on its surface, (iv) a slab of finite thickness. The following analysis is concerned only with the latter three for which a general solution of (2.13) must be found for the bulk and suitable boundary conditions applied.

The boundary condition for ferromagnets has been discussed by Mills (1971) and a similar condition

$$P'(0) = cP(0) - gh_1/nR_1 \tag{4.1}$$

is derived for percolation theory in the Appendix on the assumption that the percolation probability $P(z)$ is a slowly varying function of z. The parameters c, g and R_1 are

model dependent. g is a geometric constant. R_1 is the distance of the mass centre of the negative half of $\omega(\boldsymbol{r})$ from its centre and is the lattice parameter in the case of a cubic lattice. The parameter $c^{-1} = \lambda$ is known as the extrapolation length since it is the value of $-z$ at which linear extrapolation of $P(z)$ at the surface gives zero. It may be thought of as a variable since it depends on the expected numbers n and n_1 of ordinary and surface particles in the capture region of a particle on the surface. In case (ii), $c = 0$ when $n_1 = 0$, however in case (iii) it is positive for $n_1 = 0$ and only becomes negative when n_1 exceeds a model dependent critical value. It will turn out that the value $c = 0$ is special since for $c < 0$ the surface can percolate even though the clusters in the bulk are still finite.

A second measure of the mean size of clusters is of interest in the case of surface percolation. We define $S_0(z)$ as the mean area of intersection of the surface $z = 0$ with the domain $\omega_c(\boldsymbol{r})$ of the cluster at $\boldsymbol{r} = (x, y, z)$. In the Appendix it is shown that

$$S_0(z) = -\frac{\mathrm{d}}{\mathrm{d}h_1} \ln(1 - P(z)). \tag{4.2}$$

The equation satisfied by the percolation probability in the bulk is, from (2.13)

$$\ln(1 - P(z)) = -h - \rho \int_{\boldsymbol{r}+\boldsymbol{r}' \in \omega(\boldsymbol{r})} a(z') P(z + z')\, \mathrm{d}z' \tag{4.3}$$

where $a(z')$ is the cross sectional area of ω perpendicular to the z axis and at distance z' from its centre. Differentiating with respect to h and h_1 gives the mean size equations

$$S(z) = 1 + \rho \int_{\boldsymbol{r}+\boldsymbol{r}' \in \omega(\boldsymbol{r})} a(z')(1 - P(z + z'))S(z + z')\, \mathrm{d}z' \tag{4.4}$$

and

$$S_0(z) = \rho \int_{\boldsymbol{r}+\boldsymbol{r}' \in \omega(\boldsymbol{r})} a(z')(1 - P(z + z'))S_0(z + z')\, \mathrm{d}z'. \tag{4.5}$$

Notice that (4.5) is also satisfied by $P'(z)$ and that the solution of (4.4) has an additive part proportional to $S_0(z)$. For systems (ii) and (iii), S_0 and P' both tend to zero as $z \to \infty$ and hence

$$P'(z) = AS_0(z). \tag{4.6}$$

4.1. The non-percolating region

At sufficiently low densities in zero 'field' we shall see that there is a non-percolating region in which $P(z) = 0$. The solution for this region is identical to that obtained by Lubensky and Rubin (1975) for the ferromagnetic system since both are random walk problems. Their results were obtained by solving differential equations which may be obtained from (4.1), (4.2) and (4.3) by assuming the functions to be slowly varying (see § 4.2). Notice that when $P(z) = 0$ this may be avoided since (4.3) has solution

$$S_0(z) = B\, \mathrm{e}^{-z/\xi} \tag{4.7}$$

where ξ is determined by

$$\rho \int_{\boldsymbol{r}+\boldsymbol{r}' \in \omega(\boldsymbol{r})} a(z')\, \mathrm{e}^{-z'/\xi}\, \mathrm{d}z' = 1 \tag{4.8}$$

and the 'slowly varying' approximation is obtained by an expansion of the exponential in powers of z'/ξ to second order. The result is the same as (3.12). Determination of the constant B using

$$S_0'(0) = cS_0(0) - g/nR_1 \tag{4.9}$$

which follows from (4.1) gives Lubensky and Rubin's result

$$S_0(z) = e^{-z/\xi}(g/nR_1)\xi/(1+c\xi). \tag{4.10}$$

Since (4.4) with $P(z) = 0$ has a particular solution $S_\infty = (1-n)^{-1}$ (the uniform system solution (3.6)) the general solution may be obtained by adding a part proportional to $S_0(z)$ and using the boundary condition

$$S'(0) = cS(0) \tag{4.11}$$

thus

$$S(z) = S_\infty[1 - c\xi\, e^{-z/\xi}/(1+c\xi)]. \tag{4.12}$$

Notice that for $c > 0$, $S(0)$ diverges at the bulk critical density $n = 1$ and that $S_0(0)$ is finite but non-analytic at this point. As n increases through unity we shall see that a transition occurs to a state in which $P(z) > 0$ for all z. For $n > 1$ the whole system is in a percolating state and the transition is therefore known as an 'ordinary' transition (see § 4.2).

For $c < 0$ both $S(0)$ and $S_0(0)$ diverge when $1 + c\xi = 0$ which corresponds to a value of n less than one; near $n = 1$ the critical density n_s which corresponds to this condition is given by

$$\begin{aligned} 1 - n_s &\simeq \tfrac{1}{2} n_s R^2 |c|^{1/\nu} \\ &= \tfrac{1}{2} n_s (Rc)^2 \end{aligned} \tag{4.13}$$

where we have used (3.12). As n increases beyond n_s it will be shown that the surface undergoes a transition to a percolating state ($P(0) > 0$) but that $P(z) \to 0$ exponentially as $z \to \infty$. The 'surface' and 'ordinary' transition lines are shown in figure 1 where the

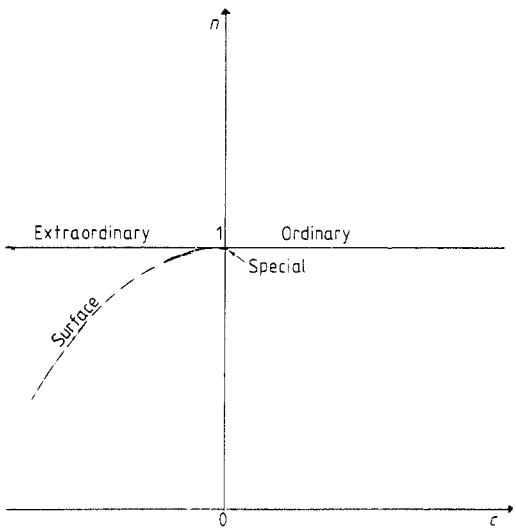

Figure 1. Schematic phase diagram.

'extraordinary' transition line ($n = 1, c < 0$) is also drawn. The latter corresponds to the onset of percolation in the bulk ($P(\infty) > 0$) in the presence of surface percolation.

From (4.12) we see that the special value $c = 0$ gives $S(z) = S_\infty$ for all z whereas $S_0(z) \sim \xi$ and has an exponentially decaying amplitude as $z \to \infty$.

The percolating regions of the phase diagram are discussed in § 4.3 along with critical exponents.

4.2. General solution of the mean field equations

In order to make progress with the case $P(z) > 0$, which will arise above a critical density of ordinary particles or when h and/or h_1 are positive, it is assumed that $P(z)$ is slowly varying with z. More specifically the factor $P(z + z')$ in (4.3) is expanded in a Taylor series about $z' = 0$ and terms higher than the second are discarded. This will be valid when the connectedness length is much larger than the width of the capture region so that the results will be asymptotically correct near the transition lines except that for the surface transition line n must also be close to one. Assuming further that the symmetry of the region ω is such that the integral of the first order term is zero we obtain

$$\lg(1 - P(z)) \cong -h - nP(z) - \tfrac{1}{2}nR^2P''(z). \tag{4.14}$$

Similar equations may be obtained for $S(z)$ and $S_0(z)$ using (4.4) and (4.5).

If P_∞ is the solution for the homogeneous problem (P_∞ satisfies (3.1)) and the loagarithm is expanded to second order (as in § 3) then the solution of (4.14) may be written in the scaling form

$$P(z) = P_\infty + \tfrac{3}{2}n(R/\xi)^2 Q(z/\xi) \tag{4.15}$$

where Q must satisfy

$$Q''(x) - Q(x) - \tfrac{3}{2}Q^2(x) = 0. \tag{4.16}$$

The phase portrait (Q' against Q) for this differential equation is shown in figure 2. The arrows indicate the direction of z increasing.

The solution curve required is selected using the boundary conditions

$$\begin{aligned} &\text{(i) for } z \to \pm\infty, && Q, Q' \to 0 \\ &\text{(ii) for } z = 0, && Q'(0) = c\xi(Q(0) + a - \hat{h}_1) \end{aligned} \tag{4.17}$$

where from (4.1)

$$a = 2P_\infty\xi^2/3nR^2 \qquad \text{and} \qquad \hat{h}_1 = 2gh_1\xi^2/3n^2R^2R_1c. \tag{4.18}$$

In the case of a slab of finite thickness D, a condition of type (ii) must be imposed at $z = \pm\frac{1}{2}D$. The surface percolation probability may be expressed in terms of $Q(0)$ and a by

$$P(0) = \tfrac{3}{2}n(R/\xi)^2(Q(0) + a). \tag{4.19}$$

From (3.4) and (3.10), a is a function of the scaled field $\hat{h} = h/(n-1)^2$, thus

$$a \cong \tfrac{1}{3}[1 \pm (1 + 2\hat{h})^{-1/2}] \qquad \text{for } n \to 1. \tag{4.20}$$

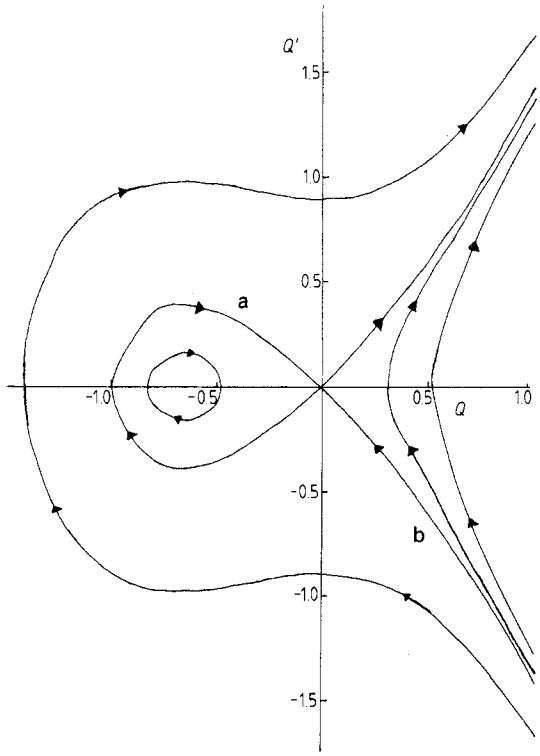

Figure 2. Phase portrait of the differential equation $Q'' - Q - \frac{3}{2}Q^2 = 0$.

Hence for all values of n and $h \geqslant 0$, a lies in the range $0 \leqslant a \leqslant \frac{2}{3}$ and in particular

$$a = \begin{cases} 0 & \text{for } h = 0,\ n < 1 \\ \frac{1}{3} & \text{for } n = 1,\ h > 0 \\ \frac{2}{3} & \text{for } h = 0,\ n > 1. \end{cases} \tag{4.21}$$

When $n < 1$, $a \to 0$ as $h \to 0$ according to the formula

$$a \cong \tfrac{1}{3}h/(1-n)^2. \tag{4.22}$$

4.3. Systems (ii) *and* (iii)

In this section we consider the systems which satisfy the boundary conditions (i) and (ii) at $z = \infty$ and $z = 0$ respectively. In both cases only the region $z \geqslant 0$ need be considered since in case (ii) the solution in the negative region is obtained by reflection. The boundary condition (i) at ∞ implies that the required trajectory in the phase plane (figure 2) must pass through the fixed point (0, 0) which limits the choice to section a or section b of the separatrix (figure 2) since the required solution must approach (0, 0) as $z \to \infty$. Integrating (4.16) we find that both sections satisfy the equation

$$Q'(x) = -Q(x)(1 + Q(x))^{1/2}. \tag{4.23}$$

Further integration yields

$$Q(x) = \begin{cases} \operatorname{cosech}^2(\frac{1}{2}x + \phi) & Q > 0 \\ -\operatorname{sech}^2(\frac{1}{2}x + \phi) & Q < 0 \end{cases} \tag{4.24}$$

where ϕ may be obtained from $Q(0)$. From now on we shall only be interested in the surface properties. These follow from $Q(0)$. The solution for other values of z is determined in terms of $Q(0)$ by (4.15) and (4.24).

To find $Q(0)$ we must simultaneously solve (4.17) and (4.23) with $x = 0$, thus

$$-Q(0)(1+Q(0))^{1/2} = c\xi(Q(0) + a - \hat{h}_1). \tag{4.25}$$

The graphical solution is shown in figure 3. The straight line L representing the RHS has slope $c\xi$ which tends to ∞ as $n \to 1$ (three typical positions for L are shown). When $h = h_1 = 0$, L passes through $(0, 0)$ for $n < 1$ and through $(-\frac{2}{3}, 0)$ for $n > 1$. The four types of solution are shown by the small circles and the transitions referred to in § 4.1 correspond to the change in solution type as the slope of L is varied. Notice that although Q jumps in crossing the 'ordinary' transition line ($n = 1$, $c > 0$), P is continuous since it is proportional to $Q + a$. The curve representing the LHS of (4.25) has slope -1 at $(0, 0)$ which is why $c\xi = -1$ is the equation of the 'surface' transition curve. For $c < 0$ and $|c|\xi > 1$ it is clear that there is a solution with $Q > 0$ which gives a positive surface percolation probability $P(0)$ but until n exceeds unity the bulk percolation probability P_∞ is zero. When $c < 0$ and $|c|\xi < 1$ the intersection having $Q < 0$ leads to a negative $P(0)$ which is meaningless as a probability so that the solution $P(0) = 0$ must be chosen. The 'extraordinary' transition which occurs when $n = 1$ and $c < 0$ corresponds in figure 3 to the limit $Q \to \infty$ since this limit is approached by the intersection of (4.23) with L for both $n < 1$ and $n > 1$.

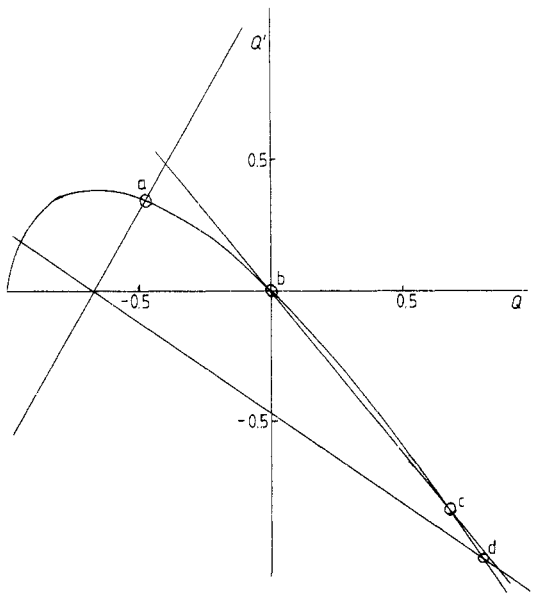

Figure 3. Graphical solution of (4.25). The four labelled cricles show the solutions corresponding to the four regions of figure 1: a, $c > 0$ and $n > 1$; b, $c > 0$ and $n < 1$, or $c < 0$ and $n < n_s$; c, $c < 0$ and $n_s < n < 1$; d, $c < 0$ and $n > 1$.

The introduction of non-zero fields corresponds to a shift in the intersection of L with the Q axis; the slope of L is independent of h_1 but depends on h through ξ. In the following paragraphs equation (4.25) is approximated to bring out the scaling form of the solutions near the transition lines. The critical exponents are also determined and are distinguished from the bulk values by superscripts s for surface, o for ordinary, e for extraordinary and sp for special. The subscripts 1 and 1, 1 denote that $z = 0$ and β_1, γ_1 and $\gamma_{1,1}$ refer to $P(0)$, $S(0)$ and $S_0(0)$ respectively. A prime on the exponent γ denotes that the high-density side of the transition is being considered although in all cases we shall find that the primed and unprimed exponents are equal. The exponents are summarised in table 1.

4.3.1. The surface transition ($c<0$, $|c|\xi \cong 1$). Near this transition it is appropriate to expand the LHS of (4.25) to second order in $Q(0)$ and solving the resulting quadratic equation gives

$$Q(0) \cong -1 - c\xi + [(1+c\xi)^2 + 2(\hat{h}_1 - a)c\xi]^{1/2}, \qquad n \to n_s. \tag{4.26}$$

This has a scaling form which is similar to that for the bulk transition (equation (3.4)) and $P(0)$ may be expressed in terms of the bulk scaling function $\hat{P}_\pm$.

$$P_{\text{sing}}(0) \cong \tfrac{3}{2} n (R/\xi)^2 |1 - |c|\xi| \hat{P}_\pm(\hat{h}_s) \tag{4.27}$$

where

$$\hat{h}_s = (\hat{h}_1 - a)c\xi(1 - |c|\xi)^{-2}. \tag{4.28}$$

The non-singular term arising from a in (4.19) has been dropped. Since ξ is non-singular as the surface transition is approached and near the transition $|1 - |c|\xi| \sim |n - n_s|$, where n_s is defined by (4.13), we find using (4.22) that

$$P(0) \cong |1 - n/n_s| P_\pm^{(s)}[h_1/(1-n/n_s)^2, h/(1-n/n_s)^2], \qquad n \to n_s. \tag{4.29}$$

The critical exponents for the surface transition are, therefore, $\beta_1^s = 1$, $\gamma_1^s = \gamma_1'^s = 1$, $\gamma_{1,1}^s = \gamma_{1,1}'^s = 1$. It may be checked that differentiation of the form of $P(0)$ obtained by substitution of (4.26) in (4.19) gives results consistent with (4.10) and (4.12) when $n < n_s$ and that when $n > n_s$ the surface mean size functions $S(0)$ and $S_0(0)$ are obtained by replacing $1 + c\xi$ by $|1 + c\xi|$.

The above exponents are the same as for the bulk transition in agreement with the view that the surface transition is like a bulk transition in one less dimension (Lubensky and Rubin 1975, Bray and Moore 1977). (Mean field exponents are independent of dimension.)

4.3.2. The ordinary transition ($n \cong 1$, $c>0$). When $h_1 = 0$ the ordinary transition corresponds to $c\xi \to \infty$ and $Q(0) \to -a$. Approximating (4.25) in this region gives the asymptotic form in the neighbourhood of the point $n = 1$, $h = h_1 = 0$ as

$$Q(0) \cong \hat{h}_1 - a - (c\xi)^{-1}(\hat{h}_1 - a)(1 + \hat{h}_1 - a)^{1/2} \tag{4.30}$$

and from (4.19), (4.18) and (4.22)

$$P(0) \cong g h_1 / n R_1 c + \xi^{-3} F[h_1 \xi^2, h/(n-1)^2] \tag{4.31}$$

which together with (3.10) implies the scaling form

$$P(0) \cong g h_1 / n R_1 c + |n-1|^{3/2} P_\pm^{(0)}[h_1/|n-1|, h/(n-1)^2]. \tag{4.32}$$

The critical exponents are therefore $\beta_1^{\circ} = \frac{3}{2}$, $\gamma_1^{\circ} = \gamma_1'^{\circ} = \frac{1}{2}$ and $\gamma_{1,1}^{\circ} = \gamma_{1,1}'^{\circ} = -\frac{1}{2}$. Notice that the finite value g/nR_1c of $dP(0)/dh_1$ at $n = 1$ agrees with (4.10) and the exponents $\gamma_{1,1}^{\circ}$ and γ_1° also follow from (4.10) and (4.12).

4.3.3. The special transition ($c = 0$, $n \cong 1$). With $c = 0$ equation (4.25) becomes

$$Q(0)(1+Q(0))^{1/2} = 2gh_1\xi^3/3n^2R^2R_1 \tag{4.33}$$

and approximating to first order in h_1 gives

$$P(0) \cong P_\infty + (gh_1/nR_1)\xi \tag{4.34}$$

which implies that $\beta_1^{sp} = 1$, $\gamma_1^{sp} = \gamma_1'^{sp} = 1$ and $\gamma_{1,1}^{sp} = \gamma_{1,1}'^{sp} = \frac{1}{2}$ (since $S_0(0) \sim \xi$). In general we have the scaling form

$$P(0) = P_\infty + \xi^{-2}\phi(h_1\xi^3) \tag{4.35}$$

$$= |n-1|P_{\pm}^{sp)}(h/(n-1)^2, h_1/|n-1|^{3/2}). \tag{4.36}$$

4.3.4. The extraordinary transition ($n \cong 1$, $c < 0$). It follows from our general discussion that the extraordinary transition occurs when $Q(0) \to \infty$ and hence $P(0)$ has a non-zero value on the transition line. This transition was originally conceived by Lubensky and Rubin (1975) to occur when n passes through its bulk critical value with $h_1 = 0$. However Bray and Moore (1977) showed that in the case of a ferromagnet a similar transition also occurs for fixed $h_1 \neq 0$ and arises from the existence of a non-zero magnetisation. The corresponding result for mean field percolation theory will now be obtained.

Equation (4.25) was obtained by expanding the logarithm in (4.14) in powers of $P(z)$. For the extraordinary transition this is inappropriate except as $c \to 0$ and we therefore return to (4.14). Integrating (4.14) and using the boundary condition (4.1) together with $P(z) \to P_\infty$ and $P'(z) \to 0$ as $z \to \infty$ gives

$$\begin{aligned} \operatorname{sgn}(c)(\psi(P_\infty) - \psi(P(0)))^{1/2} &= \tfrac{1}{2}n^{1/2}RP'(0) \\ &= \tfrac{1}{2}n^{1/2}R(cP(0) - gh_1/nR_1) \end{aligned} \tag{4.37}$$

where

$$\psi(P) = -(1-P)\ln(1-P) - P + \tfrac{1}{2}nP^2 + hP. \tag{4.38}$$

Use of (3.1) gives

$$\psi(P_\infty) = (n-1)P_\infty - \tfrac{1}{2}nP_\infty^2 + h \tag{4.39}$$

$$\cong -\tfrac{1}{2}(n-1)P_\infty^2 + \tfrac{1}{3}P_\infty^3 \tag{4.40}$$

$$\cong |n-1|^3\hat{\psi}_{\pm}(\hat{h}) \tag{4.41}$$

where the asymptotic form applies to the neighbourhood of the bulk transition point ($h = 0$, $n = 1$). Notice that $\psi(P_\infty) = 0$ for $h = 0$ and $n < 1$ but otherwise

$$\psi(P_\infty) \simeq \begin{cases} \frac{2}{3}(n-1)^3 & h = 0,\ n \to 1^+ \\ \frac{1}{3}(2h)^{3/2} & n = 1,\ h \to 0^+. \end{cases} \tag{4.42}$$

It can be seen that $\psi(P_\infty)$ has the same exponents as $\int P_\infty \, dh$ which is proportional to the mean number of clusters per unit volume in the bulk. The function $\psi(P)$ has the further

property $\psi'(P_\infty)=0$ and passes through its maximum value when $P=P_\infty$. The sign of the square root in (4.37) was chosen on the physical basis that $P'(0)$ has the sign of c.

Now define $P^-(0)$ to be the continuation of the physical solution of

$$\operatorname{sgn}(c)(-\psi(P^-(0)))^{-1/2}=\tfrac{1}{2}n^{1/2}R(cP^-(0)-gh_1/nR_1) \tag{4.43}$$

in the region $n_s<n<1$ to the region $n>1$. Notice that $P^-(0)=P(0)$ when $n_s<n<1$ and define $\delta P=P(0)-P^-(0)$ in the region $n>1$. For $h_1\neq 0$ or $h_1=0$ and $c<0$ it may be shown that $P^-(0)$ has a non-zero value when $n=1$ and also $\psi(P^-(0))$ and $\psi'(P^-(0))$ have non-zero values. Approximating (4.37) in the region of the bulk transition point gives

$$\delta P\simeq\frac{\psi(P_\infty)}{\psi'(P^-(0))+n^{1/2}|c|(-\psi(P^-(0)))^{1/2}} \tag{4.44}$$

and since $P^-(0)$ has no singularity at $n=1$ it is clear that the asymptotic form of δP is governed by $\psi(P_\infty)$ (equation (4.41)). We deduce that $\beta_1^e=3$, $\gamma_1'^e=-1$, $\gamma_{1,1}'^e=-3$. Higher derivatives of δP (and hence $P(0)$) with respect to h_1 also have the critical exponents of $\psi(P_\infty)$ since the dependence on h_1 manifests itself only via the non-singular function $\psi(P^-(0))$. Notice that we have defined the critical behaviour in terms of the part of $P(0)$ which is induced by the non-zero value of P_∞ so that γ_1^e and $\gamma_{1,1}^e$ are not defined.

4.4. System (N), the slab of finite thickness

For this system the ordinary transition takes place at a critical density n_c which is higher than that for the infinite system. The transition will be located by finding the point at which $S(z)$ diverges with $h=h_1=0$. Assuming that ξ and thickness D are large compared with the width of the capture region equation (4.4) may be replaced by

$$S(z)\pm\xi^2S''(z)=S_\infty,\qquad n\gtrless 1. \tag{4.45}$$

For $n<1$ the solution which satisfies the boundary conditions

$$S'(\pm\tfrac{1}{2}D)=\mp cS(\pm\tfrac{1}{2}D) \tag{4.46}$$

is

$$S(z)=S_\infty\left(1-\frac{\cosh(z/\xi)}{(c\xi)^{-1}\sinh(D/2\xi)+\cosh(D/2\xi)}\right). \tag{4.47}$$

This has a finite limit as $n\to 1$ since the pole in S_∞ is cancelled by a zero of the bracket. For $n>1$

$$S(z)=S_\infty\left(1-\frac{\cos(z/\xi)}{\cos(D/2\xi)-(c\xi)^{-1}\sin(D/2\xi)}\right) \tag{4.48}$$

which diverges when

$$\tan(D/2\xi)=c\xi \tag{4.49}$$

or for $c\xi\gg 1$, $\xi\simeq D/\pi$. Thus the critical density is given by

$$n_c\simeq 1+\tfrac{1}{2}n\pi^2(R/D)^2 \tag{4.50}$$

and the shift exponent λ is equal to $\frac{1}{2}$ in agreement with the scaling prediction $\lambda=1/\nu$ (Fisher and Barber 1972, Ferdinand and Fisher 1969, De'Bell 1980).

Appendix. The mean field boundary condition and the derivation of $S_0(r)$

A.1. Semi-infinite system ($z \geqslant 0$)

We suppose that the ordinary particles are distributed through the region $z \geqslant 0$ with density ρ and that in addition there is a surface density ρ_1 on the surface $z = 0$. To simplify the boundary condition we suppose that the distribution of impurity particles extends far enough into the $z < 0$ region so that the expected number of such particles in $\omega(\boldsymbol{r})$ is h, even for a point close to the surface. Additional impurity particles are distributed over the surface with density ν_1 and h_1 is the expected number of these particles in $\omega(\mathbf{0})$.

From (4.3)

$$\ln(1-P(0)) = -(h+h_1) - \int_{\substack{r' \in \omega(\mathbf{0}) \\ z' \geqslant 0}} (\rho + \rho_1 \delta(z)) a(z') P(z')\, \mathrm{d}z'$$

$$= -(h+h_1) - n_1 P(0) - \rho \int_{\substack{r' \in \omega(\mathbf{0}) \\ z' \geqslant 0}} a(z') P(z')\, \mathrm{d}z'. \tag{A1}$$

Let $P^{\mathrm{e}}(z)$ be the function $P(z)$ extrapolated into the the negative z region so as to satisfy (4.3) for all z as though there were no surface then

$$\ln(1-P^{\mathrm{e}}(0)) = -h - \rho \int_{r' \in \omega(\mathbf{0})} a(z') P^{\mathrm{e}}(z')\, \mathrm{d}z'. \tag{A2}$$

Subtracting (A2) from (A1) gives

$$\ln\left(\frac{1-P(\theta)}{1-P^{\mathrm{e}}(0)}\right) = -h_1 - n_1 P(0) + \rho \int_{\substack{r' \in \omega(\mathbf{0}) \\ z' < 0}} a(z') P^{\mathrm{e}}(z')\, \mathrm{d}z'$$

$$-\rho \int_{\substack{r' \in \omega(\mathbf{0}) \\ z' \geqslant 0}} a(z')(P(z') - P^{\mathrm{e}}(z'))\, \mathrm{d}z' \tag{A3}$$

where $n_1 = \rho_1 a(0)$. Making a linear approximation to $P(z)$ and $P^{\mathrm{e}}(z)$ over the region $\omega(\mathbf{0})$ and assuming that $P^{\mathrm{e}}(z)$ and $P(z)$ have the same value and derivative at the point where they first start to deviate gives

$$P'(0) = cP(0) - gh_1/nR_1 \tag{A4}$$

where $g = 2$,

$$c = \frac{1}{R_1}\left(1 - \frac{2n_1}{n}\right)$$

and R_1 is the distance of the centre of mass of the negative half of $\omega(\mathbf{0})$ from the origin.

A.2. The infinite system with a special plane ($z = 0$)

For this system ρ and h have the same values for all z but ρ_1 and h_1 are defined as in (A.1) in terms of additional particles on the $z = 0$ hyperplane. By symmetry $P(-z) = P(z)$ and P will be continuous. $P'(z)$ will have a discontinuous derivative with $P'(0^-) = -P'(0^+)$. Let $P^{\mathrm{e}}(z)$ be the continuation of the positive z solution as in (A.1) so

that (A2) still holds but the condition $z' \geqslant 0$ is removed from (A1), and (A3) becomes

$$0 = -h_1 - n_1 P(0) + \rho \int_{\substack{r' \in \omega(0) \\ z' < 0}} a(z')(P^e(z') - P(z'))\, dz'. \tag{A5}$$

Expanding as before using $P^{e\prime}(0^-) = P'(0^+)$ gives (A4) with

$$c = -n_1/nR_1 \qquad \text{and} \qquad g = 1. \tag{A6}$$

A.3. Lattice percolation

The continuum formulation includes bond and site percolation by correct choice of $\omega(r)$ (see Coniglio and Essam 1977) and on the assumption that $P(r)$ is slowly varying on the scale of the lattice parameter equation (A4) may be obtained. In the particular model of bond percolation described by Essam (1980, appendix IV) for a semi-infinite d-dimensional hypercubic lattice the capture region of a given site is the $2d$ nearest-neighbour bonds, R_1 is the lattice parameter, $g = 2d$ and

$$c = \frac{1}{R_1}\left(1 - 2d\frac{n_1}{n}\right). \tag{A7}$$

For the special plane problem $g = d$ and

$$c = -dn_1/nR_1. \tag{A8}$$

In this model it is assumed that the modification of particle density is restricted to bonds in the surface plane. If the density on the perpendicular bonds adjacent to the surface is also increased or, if site percolation is considered, the form of (A4) is unchanged but the calculation of c and g is more complicated.

A.4. Derivation of $S_0(r)$ from $P(r)$

Let $\omega_c^\circ(r)$ be the intersection of $\omega_c(r)$ with the plane $z = 0$ then by definition

$$S_0(r) = \frac{\langle |\omega_c^\circ(r)| E_c(r) \rangle_F}{a(0)(1 - P(r))} \tag{A9}$$

where

$$E_c(r) = \exp\left(-\int \nu(r')\gamma_c(r', r)\, dr' - \nu_1 \int_{z'=0} \gamma_c(r', r)\, dr' \right) \tag{A10}$$

and $\nu(r') = \nu$ except for the semi-infinite system with $z' < 0$ in which case it is zero. The other parts of (2.8) hold for $S_0(r)$ provided that the integral is restricted to $z' = 0$ and $v(r)$ is replaced by $a(0)$. With $h_1 = a(0)\nu_1$ this leads to

$$S_0(r) = -\frac{d}{dh_1} \ln(1 - P(r)). \tag{A11}$$

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